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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Coating Composition and the Use Thereof in the
Production of Coatings with a Rapidly Workable Surface

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(57) 11 Claims

Appl

B

A

CH

A

B

$C=C-\overset{O}{\underset{||}{C}}$

C

D

Lewis or Brønsted base - Diazabicycloundecene
p19 (cont cl. 8)

E

photoinitiators
p20 benzophenone, etc

applicant's
photo-sensitizer

Notice: This application is as filed and may therefore contain an
incomplete specification.

Canada

CCA 3254 (10-92) 41 7530-21-936-3254

Coating composition and the use thereof in the production of coatings with a rapidly workable surface

The invention relates to coating composition formulations,
5 which give rise to coatings with a rapidly workable surface. They are particularly suitable as formulations for clear and topcoat lacquers.

Coating compositions based on CH-acid compounds and
10 olefinically unsaturated compounds are known. For example, two component lacquers containing such components are described in EP-A-0 224 158. These two component lacquers are heat curable; the curing reaction is catalysed by Lewis and/or Brønsted bases. In EP-A-0 227 454, acetoacetate
15 polymers are described as crosslinking agents for acryloyl-unsaturated acrylates. Such systems are suitable for the production of various coatings.

In the production of coatings, particularly multilayer
20 coatings in the automotive sector, it is often necessary to form layers, the surface of which is rapidly curable in order to achieve the shortest possible dwell time for vehicle bodies in the painting booth.

25 Rapid curing is achieved in a known manner by UV irradiation of coating compositions containing unsaturated components. A disadvantage of this approach is insufficient crosslinking with opaquely pigmented systems in thicker layers or in concealed areas which are not reached by the
30 UV light. These disadvantages may be overcome by the use of so-called double cure systems.

It is known in the literature to use a so-called double cure system to produce such layers, which system may be
35 initially cured by UV radiation and subsequently thoroughly cured conventionally by heating. Such a system is described in EP-A-0 247 563; this is a two component system comprising a radiation-curable oligomer with at least two (meth)acrylate groups, an OH-functional polymer, a

polyisocyanate, light stabilisers and photoinitiators. Polyisocyanates are not without toxicological problems. EP-A-0 245 639 describes the production of stable, scratch resistant and solvent resistant coatings which contain opaque pigments. In addition to an unsaturated polyester, the system contains cellulose nitrate, pigments, hydroperoxides, driers and photoinitiators; in this process, the use of peroxides has attendant risks. Even thicker layers of the systems are intended to be radiation curable.

The object of the invention is to provide coating compositions which produce coatings with a rapidly workable surface which may be formulated without toxicologically questionable polyisocyanates and require no peroxides. Mechanically and chemically stable surfaces are intended to be achieved.

It has been found that this object may be achieved with a coating composition which contains:

- A) 10 - 80 wt.% of one or more compounds with on average at least two CH-acid hydrogen atoms as crosslinking agent,
- B) 10 - 80 wt.% of one or more α, β -unsaturated compounds with at least two identical or different groups of the general formula



which are linked together by the residue of a di- or polyhydric alcohol, a di- or polyamine or aminoalcohol, in which R_1 , R_2 and R_3 are mutually independently a hydrogen atom or a straight or branched alkyl residue with 1 to 10 carbon atoms, which residue may be olefinically mono- or

polyunsaturated and/or may have one or more hydroxyl groups,

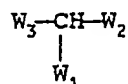
5 C) 0 - 50 wt.% of one or more radically or ionically polymerisable compounds,

10 D) 0.01 - 5 wt.%, related to the sum of the weights of components A), B), and C), of a catalyst in the form of a Lewis or Brønsted base, wherein the conjugate acids of the latter have a pKA value of at least 10,

15 E) 0.1 to 10 wt.%, related to the sum of the weights of components A), B), and C), of one or more photoinitiators, optionally together with

pigments and/or extenders, optionally together with auxiliary substances and additives customary in lacquers and optionally one or more organic solvents and/or water.

20 According to the invention, the CH-acid crosslinking agents used as component A) in the coating compositions according to the invention are those containing at least two CH-acid hydrogen atoms. These may, for example, originate from one or more of the following groupings, which may be the same
25 or different:



30 in which $W_1 =$ $\begin{array}{c} O \\ || \\ -C- \end{array}$, $\begin{array}{c} O \\ || \\ -C-O- \end{array}$, $\begin{array}{c} O \\ || \\ -C-N- \end{array}$, $\begin{array}{c} \diagup \\ -P=O \\ \diagdown \end{array}$, -CN or -NO₂;

35 $W_2 =$ $\begin{array}{c} O \\ || \\ -C- \end{array}$, $\begin{array}{c} O \\ || \\ -C-O- \end{array}$, $\begin{array}{c} O \\ || \\ -C-N- \end{array}$, $\begin{array}{c} \diagup \\ -P=O \\ \diagdown \end{array}$, or -CN;

40 $W_3 =$ $\begin{array}{c} O \\ || \\ -C- \end{array}$, $\begin{array}{c} O \\ || \\ -C-O- \end{array}$, $\begin{array}{c} O \\ || \\ -C-N- \end{array}$, H, alkyl or alkene;

wherein the carboxyl or carbonamide groups defined above for the residues W_1 , W_2 and W_3 are each bonded to the CH group via the carbon atom and the CH group is bonded via at least one of the residues W_1 , W_2 and/or W_3 to a polymeric or
5 oligomeric unit. The CH-acid functionality of component A) is on average ≥ 2 per molecule. Therefore, if W_3 in the above general formula means a hydrogen atom, then such a group is sufficient since the group has two acid hydrogen atoms.

10

As mentioned above, the CH-acid functionality of component A) is on average ≥ 2 . This means that monofunctional molecules may also be used mixed with higher-functional molecules.

15

Those CH-acid crosslinking agent compounds are preferred which are substantially free of primary, secondary or tertiary amino groups, as these can have a negative influence on storage stability and light stability.

20

Listed below are examples of CH-acid crosslinking compounds A which fall within the above general formula. These examples are subdivided below into three groups A1, A2 and A3.

25

In group A1, on average at least two groups with active H atoms of the type

30



are contained in each molecule, which groups are derived from methanetricarboxylic acid monoamide units or
35 acetoacetic acid ester-2-carboxylic acid amides.

Suitable compounds A1 are, for example, reaction products of malonic acid diesters such as dimethyl, diethyl,

dibutyl, dipentyl malonate or acetoacetic acid esters such as methyl, ethyl, butyl or pentyl acetoacetate with polyisocyanates.

reaction product A

- 5 Examples of polyisocyanates usable for this purpose are aliphatic, cycloaliphatic or aromatic polyisocyanates with at least two isocyanate groups, such as tetramethylene diisocyanate, hexamethylene diisocyanate, 2,2,4-trimethyl-hexamethylene diisocyanate, 1,12-dodecane diisocyanate, 10 cyclohexane-1,3 and -1,4 diisocyanate, 1-isocyanato-3,3,5-trimethyl-5-isocyanato-methylcyclohexane (= isophorone diisocyanate, IPDI), perhydro-2,4'- and/or -4,4'-diphenylmethane diisocyanate, 1,3- and 1,4-phenylene diisocyanate, 2,4- and 2,6-tolyene diisocyanate, 15 diphenylmethane-2,4' and/or -4,4' diisocyanate, 3,2'- and/or 3,4-diisocyanato-4-methyl-diphenylmethane, naphthylene-1,5 diisocyanate, triphenylmethane-4,4'-4'' triisocyanate, tetramethylxylylene diisocyanate or mixtures of these compounds.

20

- Apart from these simple isocyanates, those isocyanates containing heteroatoms in the residue linking the isocyanate groups are also suitable. Examples of these are polyisocyanates having carbodiimide groups, allophanate 25 groups, isocyanurate groups, urethane groups, acylated urea groups and biuret groups.

- Particularly well suited to the reaction are the known polyisocyanates which are mainly used in lacquer 30 production, for example modification products of the above-stated simple polyisocyanates containing biuret, isocyanurate or urethane groups, in particular tris-(6-isocyanatohexyl)-biuret or low molecular weight polyisocyanates with urethane groups, as may be obtained by 35 the reaction of an excess of IPDI with simple polyhydric alcohols of the molecular weight range 62 - 300, particularly with trimethylolpropane. Naturally, any

desired mixtures of the stated polyisocyanates may also be used for the production of crosslinking component A1.

Further suitable polyisocyanates are the known prepolymers having terminal isocyanate groups, as are in particular accessible by the reaction of the above-stated simple polyisocyanates, principally diisocyanates, with substoichiometric quantities of organic compounds with at least two groups capable of reacting with isocyanate groups. The compounds used to this end are preferably any such compounds having at least two amino groups and/or hydroxyl groups with a number average molar mass of 300 to 10,000, preferably 400 to 6,000. It is preferably the corresponding polyhydroxyl compounds which are used, for example the hydroxypolyesters, hydroxypolyethers and/or acrylate resins containing hydroxyl groups which are known *per se* in polyurethane chemistry.

In these known prepolymers, the ratio of isocyanate groups to hydrogen atoms reactive with NCO is 1.05 to 10:1, preferably 1.1 to 3:1, wherein the hydrogen atoms preferably originate from hydroxyl groups.

The type and quantity ratios of the starting materials used in the production of the NCO prepolymers are furthermore preferably selected such that the NCO prepolymers have a) an average NCO functionality of 2 to 4, preferably from 2 to 3 and b) a number average molar mass of 500 - 10,000, preferably from 800 - 4,000 g/mol.

Suitable compounds A1 are also, however, the reaction products of esters and partial esters of polyhydric alcohols of malonic acid with monoisocyanates. Polyhydric alcohols are, for example, di- to pentahydric alcohols such as ethanediol, the various propane-, butane-, pentane- and hexanediols, polyethylene and polypropylene diols, glycerol, trimethylolethane and -propane, pentaerythritol,

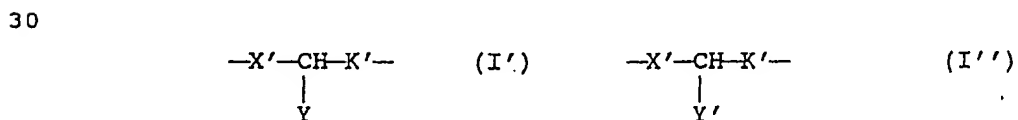
hexanetriol and sorbitol. Suitable monoisocyanates are, for example, aliphatic isocyanates such as n-butyl isocyanate, octadecyl isocyanate, cycloaliphatic isocyanates such as cyclohexyl isocyanate, araliphatic isocyanates such as
 5 benzyl isocyanate or aromatic isocyanates such as phenyl isocyanate.

Also suitable are the corresponding malonic esters and acetoacetic acid esters of acrylic resins, polyesters,
 10 polyurethanes, polyethers, polyester amides and imides containing OH groups, and/or reaction products of malonic acid semi-esters such as malonic acid monoethyl ester with aliphatic and aromatic epoxy resins, for example acrylate resins containing epoxy groups, glycidyl ethers of polyols
 15 such as hexanediol, neopentyl glycol, diphenylolpropane and -methane and hydantoins containing glycidyl groups, together with mixtures of these compounds.

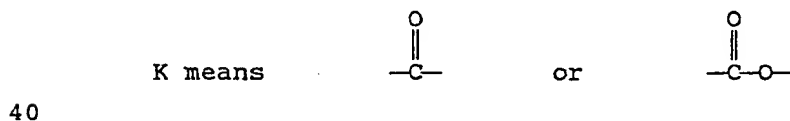
The examples of the following group A2 exhibit a suitable
 20 curing component with active CH groups, which component contains as least two groups of the formula (I)



or structural units of the formulae (I') or (I'')



35 in which:



wherein the latter group is bonded to the CH group via the C atom;

X and Y are the same or different and are

5



10 $-\text{CO}_2\text{R}^1$, $-\text{CN}$, $-\text{NO}_2$, $-\text{CONH}_2$, $-\text{CONR}^1\text{H}$ or $-\text{CONR}^1\text{R}^1$, wherein the residues R^1 may be the same or different and stand for a hydrocarbon residue, preferably an alkyl residue with 1 to 12, preferably 1 to 6 C atoms, which residue may also be interrupted by oxygen or an N-alkyl residue, with the proviso that only one of the two residues X, Y can
15 represent the NO_2 group;

K' means



or



20

wherein the latter group is bonded to the CH group via the C atom;

X' and Y' are the same or different and mean

25



or



with the proviso that, if K' and X' simultaneously mean

30



35 the residue Y' preferably does not mean



40

The number of (I) groups in the curing agent according to the invention is preferably 2 to 200 and in particular 2 to 10, wherein the higher numbers refer to oligomeric or polymeric products, in which case they are averages as 5 mixtures may be present.

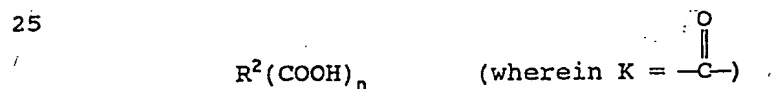
The curing component A2 usable according to the invention preferably has the formula (II)



15 in which X, Y and K have the above meaning, R^2 represents the residue of a polyol

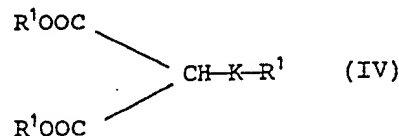
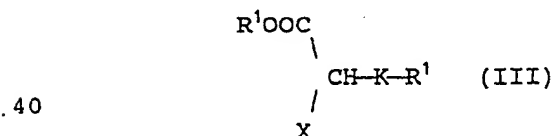


or the residue R^2 of a polycarboxylic acid



and n means at least 2, preferably 2 to 200, in particular 2 to 10. In the case of oligomeric or polymeric curing components these figures are again average values.

Also preferred are curing components coming within group A2 which are obtained by transesterification of compounds of 35 the formula (III) or the formula (IV)



with polyols $R^2(OH)_n$, wherein X, K and R^1 have the above meaning.

- The above-stated polyols $R^2(OH)_n$ may be a polyhydric
- 5 alcohol, preferably containing 2 to 12, in particular 2 to 6 C atoms. Examples of such polyols are: ethylene glycol, (1,2)- and (1,3)-propylene glycol, (1,4)- and (2,3)-butylene glycol, di- β -hydroxyethylbutanediol, (1,6)-hexanediol, (1,8)-octanediol, neopentyl glycol,
- 10 (1,6)-cyclohexanediol, 1,4-bis-(hydroxymethyl)-cyclohexane, 2,2-bis-(4-hydroxycyclohexyl)-propane, 2,2-bis-(4-(β -hydroxyethoxy)phenyl)-propane, 2-methyl-1,3-propanediol, glycerol, trimethylolpropane, (1,2,6)-hexanetriol- (1,2,4)-butanetriol, tris-(β -hydroxyethyl)-isocyanurate,
- 15 trimethylolpropane, pentaerythritol and their hydroxyalkylation products, together with diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycols, dipropylene glycol, tripropylene glycol, polypropylene glycols, dibutylene glycol,
- 20 polybutylene glycols and xylylene glycol. Those polyesters may also be used which are obtained from or with lactones, for example ϵ -caprolactone or hydroxycarboxylic acids, such as for example hydroxypivalic acid, ω -hydroxydecanoic acid, ω -hydroxycaproic acid, thioglycolic acid. In such
- 25 polyhydric alcohols the index n in the above formula (II) preferably stands for 2 to 4.

- Alternatively, the polyol may be an oligomeric or polymeric polyol compound (polyol resin), the number average
- 30 molecular weight of which, M_n (determined by gel chromatography; polystyrene standard), is customarily in the range from approximately 170 to approximately 10,000, preferably approximately 500 to approximately 5,000. In special cases, the number average molecular weight may,
- 35 however, be 10,000 and over. Polymers, polycondensates or polyaddition compounds may here be considered as oligomers/polymers. The hydroxyl value is generally 30 to

250, preferably 45 to 200 and in particular 50 to 180 mg KOH/g. These compounds containing OH groups may optionally contain further functional groups, such as carboxyl groups.

5

Examples of such polyols are polyether polyols, polyacetal polyols, polyesteramide polyols, polyamide polyols, epoxy resin polyols or their reaction products with CO₂, phenolic resin polyols, polyurea polyols, polyurethane polyols, 10 cellulose ester and ether polyols, partially saponified vinyl ester homo- and copolymers, partially acetalised polyvinyl alcohols, polycarbonate polyols, polyester polyols or acrylate resin polyols. Polyether polyols, polyester polyols, acrylate resins and polyurethane polyols 15 are preferred. Such polyols, which may also be used mixed together, are, for example, described in DE-OS 31 24 784.

Examples of polyurethane polyols are produced from the reaction of di- and polyisocyanates with an excess of diols 20 and/or polyols. Suitable isocyanates are, for example, hexamethylene diisocyanate, isophorone diisocyanate, tolylene diisocyanate together with isocyanurates, formed from three moles of a diisocyanate such as hexamethylene diisocyanate or isophorone diisocyanate and biurets 25 produced from the reaction of three moles of a diisocyanate with one mole of water. Suitable polyurea polyols may be obtained in a similar manner by the reaction of di- and polyisocyanates with equimolar quantities of amino alcohols, for example ethanolamine or diethanolamine.

30

Examples of polyester polyols are the known polycondensates prepared from di- or polycarboxylic acids or their anhydrides, such as phthalic anhydride, adipic acid etc., and polyols such as ethylene glycol, trimethylolpropane, 35 glycerol etc..

Suitable polyamide polyols may be obtained in a similar manner as the polyesters, by at least partially replacing the polyols with polyamines, such as isophorone diamine, hexamethylene diamine, diethylene triamine etc..

5

Examples of polyacrylate polyols or polyvinyl compounds containing OH groups are the known copolymers prepared from (meth)acrylic acid esters containing hydroxyl groups or vinyl alcohol and other vinyl compounds, such as for example styrene or (meth)acrylic acid esters.

10

The above polycarboxylic acids $R^2(CO_2H)_n$, wherein n is here preferably 2 to 4, may be of an aliphatic, cycloaliphatic, aromatic and/or heterocyclic nature and optionally substituted and/or saturated, for example with halogen atoms. The following are stated as examples of such carboxylic acids and their derivatives: succinic acid, adipic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid, terephthalic acid, isophthalic acid, trimellitic acid, pyromellitic acid, tetrahydrophthalic acid, hexahydrophthalic acid, di- and tetrachlorophthalic acid, endomethylenetetrahydrophthalic acid and its hexachloro derivative, 1,4- and 1,3-cyclohexanedicarboxylic acid, glutaric acid, maleic acid, fumaric acid, dimeric and trimeric fatty acids, such as oleic acid, optionally mixed with monomeric fatty acids or cyclic monocarboxylic acids, such as benzoic acid, p-tert-butylbenzoic acid or hexahydrobenzoic acid. Together with the reaction products of the above-stated polyols $R^2(OH)_n$ with cyclic carboxylic acid anhydrides.

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The curing component A2 which may be used according to the invention comprises, depending on the type of polyol or polycarboxylic acid component, higher or lower viscosity liquids or solids, which are largely soluble in at least customary lacquer solvents and preferably contain less than 5 wt.%, in particular less than 1 wt.%, of crosslinked

35

components. The CH equivalent weight, which is an indication of the quantity of groups (I) or structural units (I')/(II'') in (A2), is generally between 100 and 5,000, preferably 200 and 2,000 and the number average molecular weight M_n is as a rule between 200 and 10,000, preferably between 500 and 5,000 (determined by gel chromatography; polystyrene standard). Processes for the production of such compounds are described in more detail in EP-A-0 310 011.

10

Further examples of curing agent components usable according to the invention are those of type A3, in which the CH grouping is derived from a compound with the grouping $-\text{CO}-\text{CHR}^3-\text{CO}-$, $\text{NC}-\text{CHR}^3-\text{CO}-$, $\text{NC}-\text{CH}_2-\text{CN}$, $=\text{PO}-\text{CHR}^3-\text{CO}-$, $=\text{PO}-\text{CHR}^3-\text{CN}$, $=\text{PO}-\text{CHR}^3-\text{PO}=$, $-\text{CO}-\text{CHR}^3-\text{NO}_2$, in which R^3 is C_1-C_8 alkyl, H, preferably hydrogen. β -dioxo compounds are preferred.

The above A3 groupings may be bonded to at least one polyvalent monomeric or polymeric compound. They may, for example, be bonded to at least one compound from the group of mono- or polyhydric alcohols, polymers, polyamines and polymercaptans containing OH groups. The compounds are polyvalent in relation to the CH functional group. They may thus, for example, be produced by esterification of a polyepoxide with a $-\text{CH}$ carboxylic acid which forms the grouping, for example cyanoacetic acid. In this manner, a component A3 is obtained with two active H atoms per epoxy group. Aromatic or aliphatic polyepoxides may be used in this instance.

Suitable examples of compounds of the type A3 are ketones, such as acetylacetone, benzoylacetone, acetyl-dibenzoylmethane, together with esters of, optionally alkyl-substituted, acetoacetic acid such as α - and/or γ -methyllacetoacetic acid, or of acetone dicarboxylic acid, malonic acid units with an ester-type linkage of malonic

acid and its monoalkyl derivatives, straight chain or branched, with 1 to 3 C atoms in the alkyl residue, for example methyl, ethyl and n-butyl or also phenyl, or of cyanoacetic acid with mono- to hexahydric alcohols with 1 to 10 C atoms. The alkyl-substituted esters, for example α -methyl or α,γ -dimethylacetoacetic ester, have only one active H atom and are therefore preferably used in the form of di- or polyesters of polyhydric alcohols in order to have a sufficient number of reactive groups available.

10 Suitable alcohols for the esterification of the above acids are, for example, methanol, ethanol, butanol, octanol and/or, and this is preferred, polyhydric alcohols or polyhydroxy compounds. Further examples of A3 are, for example, acetoacetic ester, ethanediol bisacetoacetic

15 ester, glycerol tris-malonic acid ester, trimethylolpropane tris-acetoacetic ester, partial esters of these acids with polyhydric alcohols, together with corresponding esters of acrylic resins, polyesters, polyethers, polyester amides and imides containing OH groups, polyhydroxylamines,

20 together with nitriles of these acids, to the extent that they exist, for example malonic acid mono- or dinitrile, alkoxycarbonyl-methanephosphonic acid ester and the corresponding bis-methanephosphonic acid ester. The above-stated acids may also be bonded in the form of amides

25 to amines, preferably polyamines, which also include oligomers and/or polymers including amine resins, wherein aliphatic amines are preferred.

If polyamines are the starting material, compounds A3 may

30 be produced in the form of amides. Thus, for example, it is possible to start from 1 mole of an alkene diamine which is reacted with 2 moles of acetoacetic ester to form a compound which also has four H atoms activated by amide groups.

35

Reactive nitro compounds are suitable compounds for A3, for example nitroacetic acid derivatives, such as tris-

(nitroacetic acid)-glycerol ester or trimethylolpropane-nitroacetic acid ester.

- Among the compounds for A3 which form groups of the type
- 5 -CH-, diketene and its mono- α -alkyl substitution products, together with tetrahydrodioxin, should be mentioned, which may react with suitable components to form acetoacetic ester or amide groups.
- 10 The curing agent components A may be produced in customary solvents. It is favourable to use solvents which will not later disrupt production of the coating composition. It is also favourable to keep the content of organic solvents as low as possible. If the curing agent component A contains
- 15 polar groups, for example amide or urethane groupings, it may be readily dispersed in water. This may optionally also be promoted by the crosslinking components' containing neutralisable ionic groups, for example carboxyl groups, in the oligomer or polymer skeleton. Such crosslinking agents
- 20 with ionic groups may be readily dispersed in water. In this manner, the content of organic solvents may be reduced to low levels without substantially increasing the viscosity of the crosslinking agent solution.
- 25 The binder compositions according to the invention may also contain 2-acetoacetoxy-ethylmethacrylate as a reactive diluent to adjust viscosity.

- A compound is used in the binder compositions according to
- 30 the invention as a further binder component B), which compound has at least two unsaturated groups of the general formula (V) $R_1R_2C=CR_3-CO-$, in which R_1 , R_2 and R_3 are defined as in the claims. These groups may be bonded together via short or long chain residues, oligomers and/or polymers of
- 35 di- or polyhydric alcohols, di- or polyamines or aminoalcohol, wherein these oligomers and polymers may, for example, have a number average molecular weight M_n of 100 to

- 10,000. Oligomers and polymers which may, for example, be considered are saturated and/or unsaturated polyethers, polyesters or polyurethanes containing two or more hydroxyl groups, for example those based on maleic acid, phthalic acid and diols, acrylic resins containing hydroxyl groups, aliphatic or preferably aromatic epoxy resins, optionally containing hydroxyl groups, for example those based on diphenylolpropane and/or diphenylolmethane, hydantoin and/or amine resins. The residue of the general formula (V) may here be bonded with an ester-type linkage, for example by the reaction of glycidyl (meth)acrylate with carboxyl groups from acid-functional polyethers, polyesters, polyurethanes or poly(meth)acrylates or by addition of acrylic or methacrylic acid or their derivatives onto epoxy resin epoxy groups or by esterification of polyol hydroxyl groups. Suitable polyhydric alcohols are, for example, alkanediols and triols with 2 to 8 carbon atoms such as ethanediol, the various propane, butane, hexane and octane diols, or their homologues, the corresponding oligomeric ethers, together with glycerol, trimethylolethane or trimethylolpropane, hexanetriol, pentaerythritol, dipentaerythritol, sorbitol and polyvinyl alcohol together with ethoxylated and propoxylated variants.
- The groups of the general formula (V) may also be bonded via NH groups and/or OH groups to polyamines with at least two NH groups or at least one NH group and at least one OH group. Starting compounds containing NH groups for such compounds which may be stated are, for example, di- and polyamines, such as alkene diamines and their oligomers, such as ethylenediamine, propylenediamine, diethylenetriamine, tetramines and higher homologues of these amines, together with aminoalcohols such as diethanolamine or the like. Amines which may be considered are also, for example, aminocarboxylic acid esters of polyhydric alcohols. Compounds with NH groups which may be considered are, for example, acrylic or methacrylic acid

polyamides, together with polyurethanes, for example polyisocyanates, which are capped in the form of polyurethane groups, such as those obtained by the reaction of hydroxyethylacrylate with polyisocyanates, amine resins
5 such as methoxymelamines, preferably hexamethylol melamine, urea resins, wherein the residue of the general formula (V) is bonded with the -CO- grouping to the amine groups of these compounds as an amide. If these amine compounds have OH groups or hydroxyalkyl groups, it is also possible that
10 the residue of the formula (V) is bonded with an ester-type linkage or instead via an ether group to these compounds. The starting material for ether bonding of the residue of the formula (V) may be a hydroxyalkyl ester or a hydroxyalkyl amide of an unsaturated acid such as acrylic
15 acid.

The residue of the general formula (V) in component B) may be derived from a mono- or polyunsaturated monocarboxylic acid, for example with 2 to 10, preferably 3 to 6 carbon
20 atoms, such as cinnamic acid, crotonic acid, citraconic acid, mesaconic acid, dihydrolaevulinic acid, sorbic acid, preferably acrylic acid and/or methacrylic acid.

It is also possible to use adducts prepared from copolymers
25 of the compound α -dimethyl-m-isopropenylbenzylisocyanate (called m-TMI in the remainder of the text) with hydroxy(meth)acrylic monomers. The comonomers which may be used for copolymerisation with m-TMI are, for example, customary (meth)acrylic acid esters, as have already been
30 mentioned in the explanations concerning the polyols. Possible hydroxy(meth)acrylic monomers for adduct formation with m-TMI copolymers are, for example, hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate or butanediol monoacrylate. It is also possible to use addition products
35 of hydroxyethyl methacrylate onto caprolactone.

Examples of component B are hexanediol di(meth)acrylate and dipropylene glycol di(meth)acrylate and examples of tri- and tetrafunctional monomers are trimethylolpropane tri(meth)acrylate and pentaerythritol tri- or

5 tetra(meth)acrylate, together with ethoxylated and propoxylated variants. The term (meth)acrylate used here means acrylates and/or methacrylates. Examples of oligomers or prepolymers are (meth)acrylic-functional (meth)acrylic polymers, epoxy resin (meth)acrylates, for example reaction
10 products prepared from 2 moles of (meth)acrylic acid and commercial epoxy resins, such as for example Epicote® 828, polyester (meth)acrylates, amine (meth)acrylates, unsaturated polyesters, unsaturated polyurethanes, silicone (meth)acrylates or combinations thereof.

15

Component B) may contain no solvents or it may, however, contain residual solvent from its production, for example aliphatic and/or aromatic hydrocarbons. Solids content may be adjusted to desired values, for example by removing
20 residual solvent, for example by distillation, or by the addition of water or solvents which are required for the subsequent preparation of coating compositions and are described below. The same solvent is preferably used as for component A).

25

The coating compositions according to the invention may also contain as component C) in the binder component additional materials curable by high-energy radiation, which may be monomers, oligomers or polymers or copolymers.
30 They are subject to no restrictions. They may be both radically and ionically polymerisable compounds. Radically polymerisable compounds are preferred, wherein these may also favourably be present as a mixture with ionically polymerisable compounds.

35

Examples of radically polymerisable compounds are customary radiation curable compounds, which are in particular used

- in UV-curable lacquers, based on monomers, oligomers, polymers, copolymers or combinations thereof with one or more olefinic double bonds, such as, for example, acrylic acid and methacrylic acid esters. Examples of
- 5 monofunctional monomers are butyl (meth)acrylate and hydroxyethyl (meth)acrylate. Examples of difunctional monomers are diacrylates, as were listed above as examples for component B).
- 10 Vinyl compounds may, however, also be present as monomers. These may be mono- and/or polyfunctional monomers. Examples of monofunctional monomers are hydroxybutyl vinyl ether, styrene, N-vinylpyrrolidone. Examples of polyfunctional monomers are butanediol divinyl ether, cyclohexane divinyl
- 15 ether.
- (Component D) consists of catalysts in the form of Lewis bases or Brønsted bases, wherein the conjugate acids of the latter have a pK_a value of at least 10. Component D) may
- 20 consist of one or more catalysts. Lewis bases prove to be particularly suitable, such as for example those from the group of cycloaliphatic amines, such as diazabicyclooctane (DABCO), tert.-aliphatic amines, such as triethylamine, tripropylamine, N-methyldiethanolamine,
- 25 N-methyldiisopropylamine or N-butyldiethanolamine, together with amidines such as diazabicycloundecene (DBU) and guanidines, such as for example N',N',N',N'-tetramethylguanidine. Further examples are alkyl or aryl substituted phosphanes, such as for example tributylphosphane,
- 30 triphenylphosphane, tris-p-tolylphosphane, methyl-diphenylphosphane, together with hydroxy and amino functionalised phosphanes, such as for example tris-hydroxymethylphosphane and tris-dimethylaminoethylphosphane.
- 35 Examples of usable Brønsted bases are alkoxides, such as sodium or potassium ethylate, quaternary ammonium

compounds, such as alkyl-, aryl- or benzylammonium hydroxides or halides, such as for example tetraethyl- or tetrabutyl ammonium hydroxide or fluoride, together with trialkyl or triaryl phosphonium salts or hydroxides.

5

The quantity of catalysts is generally 0.01 to 5 wt.%, preferably 0.02 to 2 wt.%, related to the total solids content of components A, B and C.

- 10 The coating compositions according to the invention contain as component E customary photoinitiators, as are used for radical and ionic polymerisation. By way of example, initiators absorbing within the wavelength range of 190 to 400 nm are suitable.

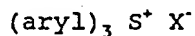
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Examples of usable radical initiators are initiators containing chlorine, such as aromatic compounds containing chlorine, for example described in US-A-4,089,815; aromatic ketones, as described in US-A-4,318,791 or EP-A-0 003 002
20 and EP-A-0 161 163; hydroxyalkylphenones, as described in US-A-4,347,111; water-soluble initiators, for example based on hydroxyalkylphenones, as described in US-A-4,602,097, unsaturated initiators such as OH-functional aromatic compounds, which have, for example, been esterified with
25 acrylic acid, as described in US-A-3,929,490, EP-A-0 143 201 and EP-A-0 341 560; or combinations of such initiators, as are, for example, described in US-A-4,017,652.

- 30 Specific examples are 2-methyl-2-hydroxy-propiophenone, benzophenone, thioxanthone derivatives, acylphosphine oxides and Michler's ketone.

- Particularly preferred usable radical initiators are
35 phosphine oxides and combinations of phosphine oxides with other customary initiators, as described above.

Examples of usable cationic initiators are triarylsulphonium salts of the general formula



5

in which aryl represents an aryl residue, such as the phenyl residue, and X^- is an anion such as SbF_6^- , PF_6^- , AsF_6^- and BF_4^- , as described in US-A-4,417,061, EP-A-0 327 194 and DE-A-2 904 626. Further examples of cationic initiators are

10 iodonium salts, oxonium salts and diazonium salts, as are, for example, described in the following references:
EP-A-0 464 131, US-A-4,421,904, EP-A-0 145 633,
EP-A-0 310 881, EP-A-0 310 882 (iodonium salts);
DE-A-3 808 590 and DE-A-3-808 591 (diazonium salts).

15

Apart from these initiators, metallocene complexes may also be used, as are, for example, described in EP-A-0 094 915.

The binder compositions according to the invention are
20 so-called two component systems.

Components A, B, C, and E are stored together as binder component 1 and component D is stored as curing agent component 2.

25

This means that components 1 and 2 are stored separately and are only mixed together just before use or for use, for example, in the production of coating compositions.

30 The coating composition formulations according to the invention may contain up to 80 wt.% of pigments and/or extenders related to total solids, including resin and curing agent.

35 Extenders which may be used are, for example, sulphates such as barium sulphate, silicas, such as pyrogenic silicas (aerosils) and silicates, such as talc.

Pigments which may be used are those customary in lacquers. These are customary opaque inorganic or organic pigments such as titanium dioxide, ultramarine blue, iron oxides and phthalocyanine blue, together with effect pigments such as,
5 for example, metallic flake pigments or pearlescent pigments.

Further auxiliary substances and additives which may optionally be used are thixotroping agents, smoothing
10 agents, flatting agents and flow-control agents.

The coating composition formulations according to the invention may contain organic solvents and/or water.

15 Suitable organic solvents for the production of coating compositions, for example lacquers, are those as may also be used in the production of the individual components A and B. Examples of such solvents are organic solvents such as aliphatic and aromatic hydrocarbons, for example
20 toluene, xylene, mixtures of aliphatic and/or aromatic hydrocarbons, esters, ethers and alcohols. These are customary lacquer solvents. Aqueous solutions may also be prepared for the production of coating compositions from the binders according to the invention. To this end,
25 suitable emulsifiers may optionally be used as are customary in the lacquers sector.

The coating compositions produced from the binders according to the invention may be adjusted to the desired
30 application viscosity by appropriate control of the addition of solvents and/or additives.

Further auxiliary substances and additives which may be added are sensitisers. These are preferably organic
35 aromatic compounds with/without heteroatoms. Examples of aromatic sensitisers without heteroatoms are anthracene and perylene. Examples of aromatic sensitisers with heteroatoms

are thioxanthene derivatives, xanthone derivatives and sulphonium complex salts.

Depending on the quantity ratio of component 1 to component
5 2, equivalent weight and catalyst quantity, the coating compositions may be adjusted to a pot life of between a few minutes and 24 hours.

Application of the coating compositions so produced may
10 proceed in a customary manner, for example by dipping, spraying, brushing or electrostatically. Subsequently, any optionally present solvents or water are vaporised by heat treatment (for example infra-red irradiation or hot air).

15 The two component coating compositions according to the invention are radiation curable after application and optionally evaporation of solvents. In particular, they are suitable for curing by irradiation with UV radiation or electron beams. Combinations of IR/UV irradiation or
20 IR/electron beam irradiation are also suitable. Radiation sources which may be used are those customary for UV or electron beam irradiation, such as high and medium pressure mercury lamps. In thicker layers, thorough curing subsequently proceeds, for example within a few hours, by
25 Michael addition.

As mentioned, after application to a substrate to be coated, the coating compositions according to the invention may rapidly be superficially cured by irradiation. By way
30 of example, curing of the surface layer up to a depth of 2 mm is possible within 10 minutes. This makes it possible to work the surface immediately, for example by sanding.

The coating compositions according to the invention have
35 the advantage that they may be formulated without solvents or with only small quantities of solvent. The coating compositions according to the invention may furthermore be

formulated such that they contain no toxic constituents, such as for example styrene.

It is naturally also possible to formulate the coating compositions according to the invention as a single component formulation without component D and to follow the radiation curing stage with thermal post-treatment at elevated temperatures of, for example, 100 - 150°C.

A particularly preferred sector for the use of the binders according to the invention is in the preparation of coating compositions for lacquer coatings in the automotive sector. Due to the favourable curing conditions of coating compositions produced from the binders according to the invention, these coating compositions are also particularly suitable for automotive repair lacquers.

The invention is illustrated with the following examples. All parts and percentages (%) relate to weight.

20

Production example 1

Production of an acetoacetic ester functionalised polyester (component A)

25 1a) Production of the polyester

336.7 parts of trimethylolpropane, 366.9 parts of adipic acid and 297 parts of hexanediol are combined with 5 parts of hypophosphorous acid in a 2 litre three-necked flask with stirrer, separator, thermometer and reflux condenser. The mixture is slowly heated from 180°C in a melt to 230°C, water being separated. The reaction is continued until an acid value of 20 mg KOH/g is reached. The mixture is then condensed under a water-jet vacuum down to an acid value of < 1.5 mg KOH/g. The resultant polyester then has an OH value of 466 mg KOH/g and a viscosity of 3200 mPa.s.

- 1b) Production of an acetoacetic-functionalised polyester on the basis of the polyester produced under 1a. 1000 parts of the polyester produced under 1a) are introduced into a 4 litre three-necked flask fitted with stirrer, dropping funnel, separator and reflux condenser. To this resin are added 850 parts of acetoacetic ester and 1.5 parts of 98% formic acid and the mixture is heated to 130°C, ethanol being separated. The resin is further heated to 165°C until a total of 400 parts of distillate have been separated. All volatile constituents are then stripped out under a vacuum. The 98.1% resin obtained then has a viscosity of 3100 mPa.s and a colour value of 65 Hazen.
- 1c) Production of trimethylolpropane triacetoacetate 670 parts of trimethylolpropane and 1950 parts of acetoacetic acid ethyl ester are introduced into a 4 litre three-necked flask fitted with a stirrer, reflux condenser, thermometer and dropping funnel. The mixture is heated while being stirred until ethanol is eliminated. After 4 hours, 488 g of distillate have been produced; the temperature is 175°C. A vacuum is applied and distillation continued until a total of 806 g of distillate have been obtained. The acetoacetic ester functional component 1c then has a theoretical solids content of 96.5%, a viscosity of 172 mPa.s and an acid value of 131.6 mg KOH/g of solid resin.

Example 2

Grafted polyester resin 2b (component B):

- 2a) Unsaturated polyester resin
- 140.0 parts of trimethylolpropane, 435.0 parts of neopentyl glycol, 370.0 parts of 1,6-hexanediol together with 409.0 parts of tetrahydrophthalic

anhydride, 294.0 parts of maleic anhydride, 352.0 parts of phthalic anhydride and 0.8 parts of hydroquinone are weighed out into a reaction vessel fitted with a stirrer, thermometer and distillation column with a water separator on top. After addition of 160 parts of xylene, the mixture is heated under a nitrogen atmosphere. At a maximum temperature of 195°C, water is removed from the system until the acid value is less than 30 mg KOH/g of solid resin. The mixture is then cooled and the distillation column replaced with a distillation bridge. The added xylene is distilled off under a vacuum at 120°C. Final values: solids (1h/150°C): 99.3%, acid value: 29.9 mg KOH/g solid resin, viscosity: highly viscous, colour value (Gardner): 2-3

2b) Grafting of 1a) with glycidyl methacrylate
In a reaction vessel with a stirrer, thermometer and reflux condenser, 2000.0 parts of polyester resin 2a) are combined with 126.6 parts of glycidyl methacrylate and 4.2 parts of triphenylphosphine and heated to 120°C under a nitrogen atmosphere. The reaction is continued at 120°C until an acid value of below 5 mg KOH/g of solid resin is achieved. The mixture is then diluted with 533 parts of pentaerythritol triacrylate. Final values: solids (1 h/150°C): 98.7%; acid value at approx. 80% in pentaerythritol triacrylate: 3.5 mg KOH/g of solid resin.

30 Grafted polyester resin 2d:

2c) Unsaturated polyester resin
378.0 parts of trimethylolpropane, 1760.5 parts of neopentyl glycol, 330.0 parts of 1,6-hexanediol, 1104.5 parts of tetrahydrophthalic anhydride, 1424.0 parts of maleic anhydride, 2.0 parts of hydroquinone and 400 parts of xylene are condensed in a manner

analogous to 1a) until an acid value of below
30 mg KOH/g of solid resin is reached.

- 2d) Grafting with glycidyl methacrylate
- 5 The polyester resin produced under 2c) is directly combined with 291.0 parts of glycidyl methacrylate and 9.0 parts of triphenyl phosphine. The temperature is maintained at 120°C until an acid value of below 5 mg KOH/g of solid resin is reached.
- 10 3) Clear lacquer:
- | | | |
|------|--|-------|
| CH { | Polyester from example 1b) | 29.0 |
| | Polyester from example 2d) | 16.0 |
| | Photoinitiator: 2-hydroxy-2-methyl-2-phenyl- | |
| 15 | propan-1-one | 5.0 |
| | Pentaerythritol triacrylate | 21.0 |
| | Commercial polyester acrylate (component B) | 28.0 |
| | Diazabicycloundecene | 1.0 |
| | | 100.0 |
- 20 4) Clear lacquer:
- | | | |
|----|--|-------|
| | Polyester from example 1c) | 40.0 |
| | Polyester from example 2b) | 22.0 |
| | Photoinitiator: 2-hydroxy-2-methyl-2-phenyl- | |
| 25 | propan-1-one | 7.0 |
| | Pentaerythritol triacrylate | 30.0 |
| | Diazabicycloundecene | 1.0 |
| | | 100.0 |
- 30 5) Topcoat lacquer:
- | | | |
|----|---|------|
| | Polyester from example 1c) | 23.0 |
| | Polyester from example 2b) | 19.0 |
| | Photoinitiator: 1-hydroxy-cyclohexyl-phenyl | |
| | ketone | 3.0 |
| 35 | Pyrogenic silicon dioxide | 0.3 |
| | Titanium dioxide | 23.0 |
| | Commercial polyester acrylate (component B) | 22.0 |

	Pentaerythritol triacrylate	8.0
	Diazaabicycloundecene	1.7
		100.0
5	6) <u>Surfacing compound</u>	
	Polyester from example 1b)	16.5
	Photoinitiator: 1-hydroxy-cyclohexyl-phenyl ketone	3.0
	Dipropylene glycol diacrylate	17.0
10	Pyrogenic silicon dioxide	0.5
	Talc	40.1
	Extender (Blancfix F)	10.0
	Titanium dioxide	2.0
	Pentaerythritol triacrylate	9.0
15	Diazaabicycloundecene	1.9
		100.0

The clear or topcoat lacquers from examples 3, 4 and 5 were applied with a coating knife to a wet film thickness of approximately 50 μm and cured by 10 minutes' irradiation with a Hönle type 250 hand lamp (distance 20 cm). The films have elevated hardness, good gloss and good petrol resistance and are tack-free after irradiation.

A 1 cm deep indentation (approximately 1.5 cm^3) was filled with the formulation described in example 6 using a spatula. The surface (approximately 2 mm) was cured by 10 minutes' irradiation with a Hönle type 250 hand lamp (distance 20 cm) and is then workable. The entire formulation then thoroughly cures overnight.

PATENT CLAIMS

1. Coating composition containing

- 5 A) 10 - 80 wt.% of one or more compounds with on average at least two CH-acid hydrogen atoms as crosslinking agent,
- 10 B) 10 - 80 wt.% of one or more α,β -unsaturated compounds with at least two identical or different groups of the general formula
- $$R_1R_2C=CR_3-CO-$$
- 15 which are linked together by the residue of a di- or polyhydric alcohol, a di- or polyamine or aminoalcohol, in which R_1 , R_2 and R_3 are mutually independently a hydrogen atom or a straight or
- 20 branched alkyl residue with 1 to 10 carbon atoms, which residue may be olefinically mono- or polyunsaturated and/or may have one or more hydroxyl groups,
- 25 C) 0 - 50 wt.% of one or more radically or ionically polymerisable compounds,
- 30 D) 0.01 - 5 wt.%, related to the sum of the weights of components A), B), and C), of a catalyst in the form of a Lewis or Brønsted base, wherein the conjugate acids of the latter have a pKA value of at least 10,
- 35 E) 0.1 - 10 wt.%, related to the sum of the weights of components A), B), and C), of one or more photoinitiators, optionally together with

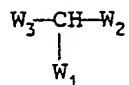
pigments and/or extenders, optionally together with auxiliary substances and additives customary in lacquers and optionally one or more organic solvents and/or water.

5

2. Coating composition according to claim 1 containing a crosslinking agent component A) with on average at least two CH-acid hydrogen atoms which originate from one or more of the following groupings, which may be

10

the same or different:



15

in which $W_1 =$ $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}- \end{array}$, $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{O}- \end{array}$, $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{N}- \end{array}$, $\begin{array}{c} \diagup \\ \text{P}=\text{O} \\ \diagdown \end{array}$, $-\text{CN}$ or
or $-\text{NO}_2$;

20

$W_2 =$ $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}- \end{array}$, $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{O}- \end{array}$, $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{N}- \end{array}$, $\begin{array}{c} \diagup \\ \text{P}=\text{O} \\ \diagdown \end{array}$, or $-\text{CN}$;

25

$W_3 =$ $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}- \end{array}$, $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{O}- \end{array}$, $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{N}- \end{array}$, H, alkyl or
alkene;

30

wherein the $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{O}- \end{array}$ and $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{N}- \end{array}$ are each bonded to the CH group via the carbon atom and the CH group is bonded via at least one of the residues W_1 , W_2 and/or W_3 to a
polymeric or oligomeric unit.

35

3. Coating composition according to claim 1 or 2, characterised in that it is in solvent-free form.

40

4. Coating composition according to claim 1 or 2, characterised in that it is in a form containing solvent.

5. Coating composition according to claim 1 or 2, characterised in that it is in the form of an aqueous solution.
- 5 6. Coating composition according to one of claims 1 to 5, characterised in that it contains one or more sensitisers.
7. Coating composition according to one of claims 1 to 6
10 in the form of a clear lacquer without pigments or a topcoat lacquer containing pigments.
8. Process for the production of a coating, characterised
15 in that a coating composition according to one of claims 1 to 7 is applied to a substrate to be coated, the surface of the film obtained is cured with high-energy radiation, in particular UV radiation, and the deeper layers are then allowed to cure thoroughly at room temperature or with heating.
- 20 9. Use of the coating composition according to one of claims 1 to 7 for the production of coatings with a rapidly curing surface.
- 25 10. Use of the coating composition according to one of claims 1 to 7 as a clear lacquer or topcoat lacquer or filler.
- 30 11. Use of the coating composition formulation according to one of claims 1 to 7 for the production clear or topcoat lacquer coating layers in multi-layer lacquer coatings, in particular in motor vehicle or motor vehicle component lacquer coatings.